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SURFACE CHARACTERISTICS OF MATERIALS BASED ON SODIUM LIQUID GLASS MODIFIED BY POLYVINYL ALCOHOL AND POLYVINYLPIRROLIDONE

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Sorption properties of materials based on sodium liquid glass modified by polyvinyl alcohol and polyvinylpyrrolidone on regarding to different acid-base indicators were investigated. The effect of the nature of metal and polymer modifier (polyvinyl alcohol and polyvinylpyrrolidone) on the amount of active centers and specific active surface area of such material was determined. Moisture absorption of modified and not modified silicate materials was founded. The effect of Ni-containing polymer-silicate materials on the speed of curing of compositions based on unsaturated polyester resins was determined.

Key words: modifier, polyvinylpyrrolidone, polyvinyl alcohol, sorption, indicators, moisture absorption, polyester resin.

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ПОВЕРХНЕВІ ХАРАКТЕРИСТИКИ МОДИФІКОВАНИХ ПОЛІВІНІЛОВИМ СПИРТОМ І ПОЛІВІНІЛПІРОЛІДОНОМ МАТЕРІАЛІВ НА ОСНОВІ НАТРІЄВОГО РІДКОГО СКЛА

Досліджено сорбційні властивості модифікованих полівініловим спиртом і полівінілпіролідом матеріалів на основі натрієвого рідкого скла щодо різних кислотно-основних індикаторів. Визначено вплив природи металу і полімерного модифікатора (полівінілового спирту та полівінілпіролідону) на кількість активних центрів та питому площу активної поверхні таких матеріалів. Встановлено значення вологопоглинання для модифікованих та не модифікованих силікатних матеріалів. Виявлено вплив модифікованих Ni-вмісних полімер-силікатних матеріалів на швидкість тверднення композицій на основі ненасичених поліестерних смол.

Ключові слова: модифікатор, полівінілпіролідон, полівініловий спирт, сорбція, індикатори, вологопоглинання, поліестерна смола.

Introduction

Of increasing importance for all sectors of the economy are polymer composite materials for which is typical filler with a set of properties: acid-base balance of the surface, selective sorption ability, nano-size, technological compatibility with the matrix of polymer, etc [1, 2]. From a large number of fillers that using to create polymer composites well have shown themselves silicate materials of various nature based on colloidal

silicon dioxide and layered clay [3, 4]. In particular, it is expedient to use silicate fillers obtained on the basis of sodium liquid glass and metal salts, which allows obtaining metal-containing silicate materials with a wide range of possible applications. Creating of composites have problem of ensuring sufficient technological compatibility of the filler and polymer matrix, which decrease leads to deterioration of physical and mechanical properties [5]. Preferably, the

previous modification of the fillers of polymeric composite materials by physical or chemical methods by compounds of various nature [6, 7]. The development and research of modified fillers for polymer composite materials is one of the priority directions of the technology of polymer and composite materials [8].

The primary problem that arises when creating such materials is to ensure the technological compatibility of the inorganic filler to the polymer matrix, which allows not only to provide special characteristics to such composites, but also leads to improvement of their physico-mechanical and thermophysical properties.

Obviously, an important characteristic of such modified fillers is the properties of their surface: the number of active centers q_a and the value of the area of the active surface S_a , which are directly related to the process of their obtaining and modification, as well as the nature of the modifier [9].

The purpose of this work is to establish the laws of the influence of the method of obtaining metal-containing polymer-silicate fillers and the nature of the polymer modifier on their surface properties.

Materials and methods of research

Due to physical-chemical regularities of the process of obtaining metal-containing polymer-silicate materials (MPSM) used two methods of they obtain. According to the first method, a solution of PVP was prepared in Na-LG, which was acted with solutions of metal chlorides; according to the second, were prepared solutions of metal chlorides with dissolved PVA, which acted on Na-LG [10, 11]. The resulting finely divided filler was filtered, vacuumed and washed thoroughly with distilled water, and then dried in a vacuum dryer for 90 °C.

To determine the sorption characteristics of these materials, a number of indicators were selected (diamond green, bromophenol blue, bromocresol purple, methylene blue, indigocarmin, methyl orange), which differ in nature of functional groups, as well as the value of pK_a [12]. The sorption capacity of the materials was determined photocolometrically on a photocolimeter of KFK-2. Concentration of indicators in aqueous or water-alcohol solution was $(0,2-5,0) \cdot 10^{-4}$ M, and the mass of the samples

0.25 g. The material was stirred in an indicator solution for 1 hour at $(25 \pm 1)^\circ\text{C}$, after which the solution was centrifuged and the optical density was measured.

To determine the moisture absorption of silicate fillers, steam was used for a saturated solution of sodium hydroxide with a constant value of relative humidity of 95 %.

To determine the moisture absorption of silicate fillers, steam of sodium hydroxide for a saturated solution with a constant value of relative humidity of 95 % was used.

To study the influence of polymer-silicate filler on the speed of curing of polyester resins, unsaturated polyester resins of brands Estromal 11. LM-02 and Estromal A023 were used.

Investigation of the influence of polymer-silicate filler on the patterns of hardening of unsaturated polyester resins was carried out by changing the viscosity of polyester composites on Rheomat-30 at a constant shear rate 28.5 s^{-1} . The dosage amount of the test composition was placed in a measuring cell consisting of a system of coaxial cylinders.

Research results and their discussion

The influence of polymer modifiers on the surface characteristics of metal-containing PSMs was confirmed by studies of sorption of seven acid-base indicators that differ in nature of functional groups and values of pK_a and are capable of adsorption on the surface of the PSM due to physical interaction with acid-base centers.

Based on patterns of sorption found that the sorption capacity for the studied material has a specific and selective nature and determined by the nature of polymer modifier and metal (Table 1).

Table 1

The influence of the metal nature on the value of the specific active surface area of the S_a and the number of active centers q_a of MPSM

No	Ion metal	$q_a \cdot 10^6$, mol/g	S_a , m^2/g
1	Cu^{2+}	94.0	73.59
2	Ba^{2+}	77.8	60,94
3	Al^{3+}	94.6	74.06
4	Ni^{2+}	99.1	77.58
5	Zn^{2+}	96.4	75.46
6	Fe^{3+}	96.2	75.31
7	Co^{2+}	85.4	66.85

It was established that the specific area of the active surface (S_a) and the number of active centers (q_a) on it decreases in the row: $Ni^{2+} > Zn^{2+} > Fe^{3+} > Cu^{2+} > Co^{2+} > Ba^{2+}$. Such regularities are related with the peculiarities of the structure of silicate materials. And in the case of Ba^{2+} it is also related with the formation of soluble $Ba(OH)_2$ in the reaction medium and steric interference due to a large size of Ba^{2+} cation. At the same time, the influence of the valence of metal on the sorption capacity of metal-containing silica fillers is not observed, which confirms the physico-chemical homogeneity of the surface of such materials.

It is established that the number of active centers of sorption modified MPSM significantly depends on the nature of the indicators (Table 2).

Table 2

Influence of the nature of the indicator and the polymer modifier on the number of active centers of the Cu-containing polymer-silicate filler

No	Indicator	pK α	Modifier	$q_a \cdot 10^6$, mol/g
1	Diamond green	1.3	–	8.64
			PVP	7.84
			PVA	5.00
2	Bromphenol blue	4.2	–	6.36
			PVP	6.63
			PVA	–
3	Bromocresol purple	6.4	–	1.71
			PVP	0,88
			PVA	1.17
4	Methylene blue	9.7	–	94.00
			PVP	80,75
			PVA	87.10
5	Indigo carmine	12.8	–	2.28
			PVP	0,55
			PVA	1.58

As in the case of modified materials, as well as unmodified, the greatest activity is shown in relation to methylene blue and diamond green, and the lowest – bromocresol purple. At the same time, the sorption of methyl orange does not occur at all.

The use of polymer modifiers – PVP and PVA leads to a decrease in the number of active centers, with the exception of bromophenol blue. Thus feature of sorption is associated with the blocking of active surface groups of silicate formations (silanediol, silanol, siloxane) due to

physico-chemical interaction with functional groups of a polymer modifier. For indicators with pK α of 4.2–12.8, the effect of PVP is more pronounced than the effect of PVA. This difference is associated with higher conformational parameters of PVP macromolecules and enhanced complexation ability.

It is established that the nature of the modifier also affects the value of the specific surface area of the active surface of metal-containing polymer-silicate fillers (Fig. 1).

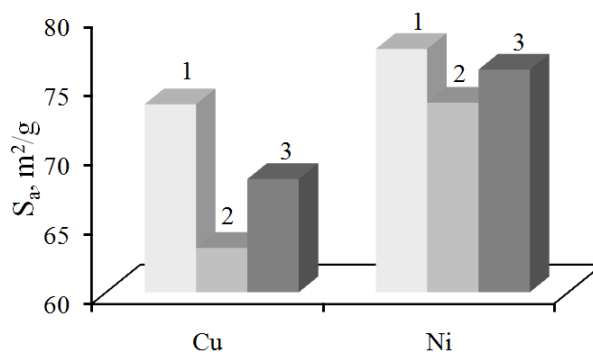


Fig. 1. The influence of the polymer modifier on the value of the relative area of the active surface: 1 – without the modifier; 2 – modifier PVP; 3 – modifier PVA

It was found that modification leads to a decrease in the value of the area of active surface relative to methylene blue not depending on the nature of the metal and the modifying effect of polyvinylpyrrolidone is more pronounced.

The influence of the concentration of polymer modifiers in the reaction medium during the production of PSM on the number of active centers of Ni-containing PSM relative to the indicator of methylene blue was established (Fig. 2).

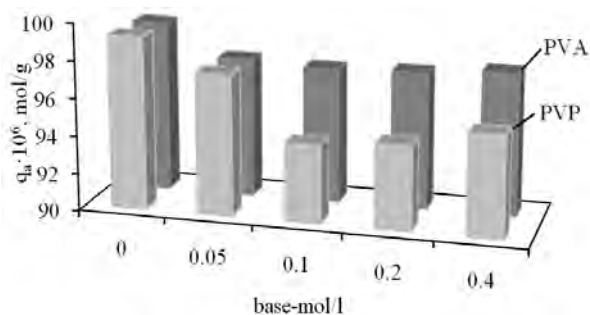


Fig. 2. Influence of nature and concentration of polymer modifier on the number of active centers of Ni-PSM

The largest decrease in the number of active centers is observed in the case of concentrations of a polymer modifier in the reaction medium in the range of 0.1–0.2 base-mol/l. It is at such concentrations that the maximum efficiency of the modification of silicate formations is achieved and the blocking of the active acid-base centers of the surface of the silicon-oxide carcass by active groups of the polymeric modifier occurs [13].

The established regularities of the influence of the nature of the polymer and the method of its introduction on the morphology and the properties of metal-containing polymer-silicate materials are to some extent confirmed by the results of the sorption studies of moisture absorption, which are given in Table 3 and in Fig. 3.

Table 3

Sorption moisture absorption of metal-containing PSM

Polymer modifier	Method of modifier input	Ion metal			
		Cu ²⁺	Ba ²⁺	Zn ²⁺	Co ²⁺
		Moisture absorption, %			
without modifier		52.4	20,2	37.5	39.5
PVP	in a solution of metal chloride	27.1	6.8	23.6	26.7
	in Na-LG	25.5	12.6	17.3	16.2
PVA	in a solution of metal chloride	28.9	7.2	32.7	32.3
	in Na-LG	29.0	16.9	34.7	19.9

Note that the nature of the metal in different ways affects the values of moisture absorption. The least value of moisture absorption is observed for systems in which the barrier chloride was used as the precipitant, which is due to the peculiarities of the interaction of the metal with Na-LG during the reaction of the formation of metal-containing polymer-silicate materials.

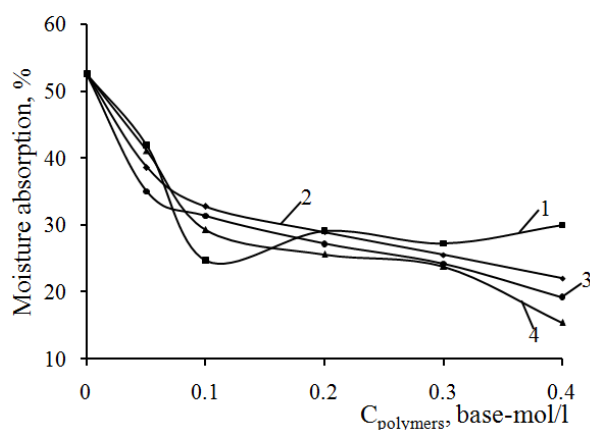


Fig. 3. Influence of the concentration of polymer and the method of its introduction on moisture absorption of Cu PSM: 1,2 – PVA; 3, 4 – PVP; method of introducing a polymer: 1,4 – in Na-LG; 2, 3 – in a solution of metal chloride

Based on the carry out sorption studies on moisture absorption, it can be concluded that the

obtained materials are characterized by a highly developed active surface. It should be noted that modified silicate materials, regardless of the nature and introduction method of the polymer modifier have markedly lower value of moisture absorption than unmodified.

This is due to the blocking of superficial groups of silicate formations (silanol and silanediol) by macromolecules of PVA and PVP, which take an active part in sorption processes H₂O.

In this case, the nature of the metal in different ways affects the value of the sorption moisture absorption of PSM, which is associated with different acid-basic properties of metals in silicon-oxygen frames.

It was established that even at low concentration of polymer there is a significant decrease in moisture absorption, which indicates an increase in the surface hydrophobicity.

Due to the fact that the developed metal-containing PSFs are marked by high values of the hydrophobic active surface area and the number of active centers on it, it was interesting to investigate the effect on the specific properties of composite materials based on thermosetting matrices.

The obtained PSMs can be used to create composite materials based on unsaturated

polyester resins, which are widely used in various fields of modern technology.

It was found that fine-dispersed metal-containing polymer-silicate materials lead to changes in the kinetic dependences of hardening of polyester compositions that were evaluated on the basis of viscometric studies.

It was found that Zn- and Co-containing PSFs slow down the hardening of unsaturated polyester oligomers, while the Ni- and Cu-content accelerates (Fig. 4).

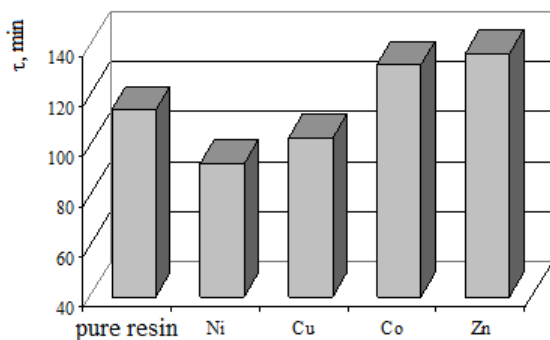


Fig. 4. Influence of the metal nature of PSM at the time of achieving a viscosity of 40 Pa·s polyester compositions during their hardening

This is due to the different activity of metals in terms of the impact on the individual stages of the resin hardening process, especially on the activation stage, and the different nature of the functional surface-active groups of fine-dispersed metal-containing PSM.

The influence of the polymer modifier of Ni-containing PSM on the patterns of hardening of unsaturated polyester resins (Fig. 5) was established.

Introduction to the reaction medium the Ni-containing polymer-silicate materials leads to an accelerated process of hardening of polyester compositions.

Polymer modifier accelerates the process of polyester matrix structure, which is due to increased technological compatibility between the components of the composite and the interactions of active carbamate groups of PVP or hydroxyl groups of PVS with components of polyester compositions. At the same time, PVP to a greater extent accelerates the process of structuring polyester compositions than polyvinyl alcohol.

It should be noted that with the decrease of the area of the active surface of the PSM and the

number of active centers on it, due to the blocking of the functional groups of the silicon-oxygen carcass by the active groups of the polymer modifier, the acceleration of the hardening of the polyester compositions is accelerated.

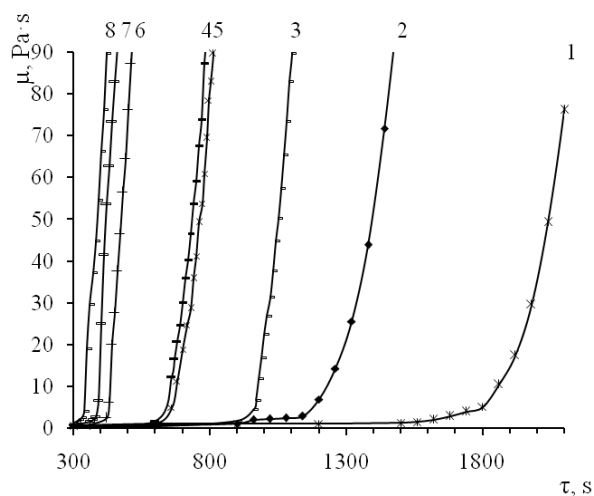


Fig. 5. Kinetic dependence of the viscosity of compositions of polyester resin Estromal 11LM-02 (1-4) and Estromal A023 (5-8) during their hardening in the presence of Ni- PSM (2 % by weight): 1, 5 – without PSM; 2, 6 – unmodified SM; 3, 7 – PSM modified by PVA; 4, 8 – PSM modified by PVP

The process of formation of a spatial polymer is accompanied by significant shrinkage and the emergence of structural inhomogeneities, which, in turn, cause the appearance of residual stresses in the matrix of the composite and affect its strength. Introduction to the composition of polyester composition of metal-containing polymer-silicate materials can influence the process of structuring coherent due to the formation of a boundary layer with a lower degree of structuring, as well as reduce the value of technological shrinkage and directed to regulate the complex of operational and technological characteristics.

Conclusions

The influence of the polymer modifier and the nature of the metal on the sorption characteristics of metal-containing polymer-silicate materials was established. It was found that the specific surface area of the active surface and the number of active centers on it depend on the nature of the metal. The greatest values of these parameters are observed for Ni^{2+} , and the smallest for Ba^{2+} and Co^{2+} .

The use of polymer modifiers, regardless of the nature of the metal and the indicator, leads to a decrease in the number of active centers and the specific surface area of the active surface, which is due to the blocking of the active groups of the surface of silicate formations due to interaction with the functional groups of the polymer modifier.

Modified silicate fillers are markedly less moisture absorption than unmodified, due to the growth of their hydrophobicity under the influence of the macrochains of the modifier, which will provide increased technological compatibility of silicate fillers to the polymer matrix during the creation of composite materials.

It was established that the introduction of Ni-containing polymer-silicate filler into polyester compositions leads to accelerating their hardening, while polymer modifiers contribute to the growth rate of this process.

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